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AMMONIUM NITRATE EXPLOSIVES CONTAINING NITROALKANES

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This invention relates to novel low cost explosives and a method for their manufacture. More particularly, this invention relates to novel explosives containing a major quantity of ammonium nitrate in the form of prills and in addition a solution comprising either a liquid hydrocarbon admixed with a nitroalkane compound, a liquid hydrocarbon admixed with a nitroalkane compound and a coupling agent such as a ketone, or a ketone per se.

In the use of explosives, the need for safety is a problem which is ever present with workers in the field. Many explosives used in the field are compounded into a finished form at the factory and shipped from there to the point of use. During shipment, special precautions must be taken. Frequently, these precautions involve limitations on the routing of the explosives and the type of carrier, etc. Further, there are limitations as to the manner in which the explosives can be shipped and stored.

As a result of these requirements regarding shipping, storage, etc., dynamite and other sensitive explosives are quite expensive to ship and store. This is reflected by a relatively high cost for the explosive material which must be borne by the ultimate user.

In many applications in the field, it is desirable to detonate an explosive in a small bore hole which is drilled in the rock or other material to be blasted. Since ammonium nitrate-fuel oil explosives require a large diameter bore hole (in excess of two inches in diameter), they are unsuitable for such operations. In these instances, dynamite must be employed since it will detonate in a small diameter bore hole.

In present blasting operations it is frequently necessary to have on hand two types of explosives. The first type is the ammonium nitrate-fuel oil explosive which requires a relatively large diameter hole in which to detonate and which requires a booster charge of dynamite or other sensitive material for initiation. The second type of explosive is dynamite which is relatively expensive and dangerous to work with. This explosive is frequently used as a booster for ammonium nitrate-fuel oil explosives and is further used alone for blasting operations which require the use of small diameter bore holes. Thus, present blasting operations always require the presence of large quantities of a relatively sensitive explosive, such as dynamite, which must be transported and stored as an explosive. This creates constant safety hazards. Also, because they should be stored separately, the use of two types of explosives creates storage and handling problems at the blasting site.

Many explosives are solids which are formed into a given shape in their manufacture. An illustration of this is the fact that dynamite generally comes in the form of sticks. By reason of their shape it is frequently difficult to get the desired quantity of explosive into the bore hole. In order to meet this problem, it is common practice in the field to slit the dynamite cartridges and tamp the explosive after it is inserted into the bore hole. This breaks down the sticks and forces the explosive into contact with the wall of the hole to get maximum packing density in the hole. Tamping is a time consuming and inherently dangerous operation since many explosives are somewhat shock sensitive.

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In order to meet the above problems, it is an object of our invention to provide a low cost multipurpose explosive which is as cheap as ammonium nitrate-fuel oil explosives from a cost effectiveness standpoint (amount of rock removed per cost of explosive, drilling the bore holes, etc.,) but which at the same time has properties which make it useful for applications now performed by dynamite. It is a further object of this invention to provide an explosive composed of ingredients which in themselves are not explosives so that they can be shipped and stored as ordinary articles of commerce. A still further object of this invention is to provide an explosive which does not require a sensitive high explosive booster, which will propagate readily in a small diameter bore hole, and which is free flowing so that it normally does not require tamping. Another object of this invention is to provide a method for compounding an explosive which method can be readily practiced in the field by inexperienced personnel without the use of elaborate mixing equipment. Additional objects will become apparent from the specification and claims which follow.

Our explosive composition comprises ammonium nitrate prills which are from about 25 to about 100 percent saturated (if 100 percent saturated, the prills are first evacuated in vacuo) with a solution containing a liquid hydrocarbon in admixture with a liquid nitroalkane; a mixture of a liquid hydrocarbon with a liquid nitroalkane and a coupling agent such as a ketone; or a ketone per se. Depending upon the particular type of ammonium nitrate prills employed, the saturation point ranges from about 13 to about 25 percent by weight of the total explosive formulation. In some cases we employ sufficient liquid sensitizer to flood the ammonium nitrate prills; that is, to fill the voids or interstices between the prills in addition to saturating them. Although this has the disadvantage of reducing the sensitivity and making the explosive more difficult to detonate, it increases the bulk density of the explosive. This has the advantage of putting more explosive in a given volume. Also, it has an advantage in underwater demolition since an increase in the bulk density of the explosive above that of the surrounding water makes the explosive sink. In underwater demolition, we place our explosive in a water resistant container, preferably a plastic bag such as polyethylene. This prevents the water from coming into contact with it and having an adverse effect upon its properties.

The liquid nitroalkane employed is a compound or mixture of compounds having the formula $R-NO_2$ in which R is a lower alkyl group such as methyl, ethyl, n-propyl, and isopropyl. Compounds included within this formula are nitromethane, nitroethane, nitropropane, and nitrobutane. Nitromethane is a preferred nitroalkane sensitizer since it has been found that our explosive compositions produced by using this compound have a higher brisance than other of our explosive compositions containing higher nitroalkanes.

The liquid nitroalkane, as defined above, is admixed with a liquid hydrocarbon which can be an aromatic, an aliphatic, or alicyclic compound or a compound which contains combinations of the above groups such as is compounds containing aralkyl, alkaryl, or cycloalkyl aryl groups. Typical of such liquid hydrocarbons are benzene, toluene, xylenes (either pure or mixed), hexane, octane, heptane, cycloheptane, methyl cyclohexane, and the like. Typical of such liquid hydrocarbons are mixed petroleum products such as gas oils, furnace oils, residual fuel oils, natural gasoline, jet fuels, kerosene, ligroin, and the like. The only requirement for the liquid hydrocarbon is that it form a solution when admixed with a liquid nitroalkane, either with or without a coupling agent as defined subsequently.

Although not bounded by any theory, it is our belief that our explosive compositions are formed through an absorption mechanism in which the liquid sensitizer material (a solution of a liquid nitroalkane, a liquid hydrocarbon, and a coupling agent; a solution of a liquid hydrocarbon and a liquid nitroalkane; or a ketone per se) migrates from the exterior surfaces of the ammonium nitrate prills into their interior portions. The liquid component of our explosive is thus uniformly distributed throughout the interior of the solid ammonium nitrate prills. As a result, our explosives are extremely powerful, easy to detonate, and vastly superior to prior art explosives in which ammonium nitrate is admixed with a fuel oil.

In order that the liquid sensitizer component of our explosives is uniformly distributed within the interior of the ammonium nitrate prills, it is necessary that the liquid sensitizer exist as a homogeneous material. In certain instances, a mixture of a liquid nitroalkane and a liquid hydrocarbon exists as a homogeneous solution. For example, benzene, toluene, hexane, and xylenes form solutions with liquid nitroalkanes such as nitromethane. In other instances, however, a liquid hydrocarbon and the liquid lower alkane are not miscible in the desired proportions. In this case, it is necessary to employ a third component in the liquid sensitizer which is termed a coupling agent. The function of the coupling agent is to solubilize the mixture of the liquid hydrocarbon with the liquid nitroalkane so as to form a true solution which is homogeneous throughout.

Typical coupling agents which may be employed in our explosive compositions are solvents such as alcohols, ketones, ethers, aromatics such as benzene and naphthalene, and mixtures of these. Preferred coupling agents are the organic ketones which are preferably dialkyl ketones. More preferably, the alkyl groups are lower alkyl groups such as methyl, ethyl, propyl, butyl, amyl, and hexyl. Typical coupling agents are dimethyl ketone, methyl ethyl ketone, diethyl ketone, diisopropyl ketone, benzene, diethyl ether, diisopropyl ether, methyl alcohol, butyl alcohol, methyl isobutyl ketone, and the like. The coupling agent can be present up to about 50 percent by weight of the liquid sensitizer material. Preferably, however, the coupling agent is present from about 5 to about 20 percent by weight of the total liquid sensitizer material.

Further, we have found that certain ketones (generally dialkyl ketones) are effective in their own right in sensitizing ammonium nitrate prills so as to form an explosive composition. These explosives are generally not as desirable as our other explosives in which the ammonium nitrate prills are sensitized with either a mixture of a nitroalkane and a liquid hydrocarbon or a mixture of a nitroalkane with a liquid hydrocarbon and a coupling agent. The latter explosives generally have a higher brisance than do our explosive compositions in which the sensitizer is only a ketone. Typical of such ketones are methyl ethyl ketone, cyclohexanone, ethyl isopropyl ketone, and the like.

The ammonium nitrate prills used in our explosives are standard items of commerce and are used widely as fertilizers. By prilled we mean that the ammonium nitrate takes the form of spheroids as produced by dropping a super-saturated solution of ammonium nitrate through a shot tower through a countercurrent flow of dry air. The individual spheres of ammonium nitrate generally range in size from about 2000 to about 5000 microns in diameter. Although the particles are not completely uniform they are generally spherical in nature and are porous with respect to our liquid sensitizer. As purchased, the ammonium nitrate prills are generally coated with an anticaking agent. The anticaking agent generally has little if any effect on the effectiveness of our explosives. Thus, our invention encompasses explosives in which either coated or uncoated prills of ammonium nitrate are used. Preferably, the ammonium nitrate prills are relatively

uniform in size since we have found that such prills give a superior explosive. Nonuniform prills also give an explosive composition, however.

The explosive compositions of our invention have an oxygen balance ranging from about -25 to about +25. Thus, when using a mixture of nitroalkanes in our explosive, a large enough percentage of an oxygen-rich lower alkane, e.g., nitromethane, is employed to counterbalance oxygen-poor ingredients in our explosive.

Our explosives are readily mixed at the site by pouring the liquid sensitizer, as defined above, onto and through the prilled ammonium nitrate. Preferably, sufficient liquid sensitizer is added so as to substantially saturate the prills. This can be readily accomplished by adding excess liquid and pouring off the excess after the prills have soaked for a few minutes or longer. Since the quantity of liquid absorbed by the prills is determined by their porosity, it is not necessary for the worker to weigh the ingredients or perform any calculations in formulating the explosive. Rather, all he has to do is add the liquid sensitizer until the prills are saturated and then pour off the excess liquid. In one typical case, approximately one gallon of sensitizer per 50 pounds of ammonium nitrate prills gives an acceptable explosive.

In order to obtain best results, our explosive compositions should not be allowed to stand for any prolonged period of time in contact with air. When this happens an appreciable quantity of the liquid sensitizer can evaporate off to give a less effective explosive. In order to prevent this from happening, the explosive should be used within a few hours after mixing or else stored in a vapor-tight container so as to prevent evaporation of the liquid sensitizer.

Incorporated into our liquid sensitizer is a dye which colors the prills after the sensitizer is mixed with them. A particular dye which we employ is Brilliant Oil Yellow #2625 as manufactured by National Aniline Corporation. Because of the color of the dye, the prills take on the color of the dye when they are saturated with the sensitizer. This informs everyone dealing with the material that the explosive is ready for use and should be treated as an explosive. After the explosive has set for some time so that a portion of the sensitizer has evaporated, the yellow dye takes on a red color on the surface of the mixed explosive. This indicates to people dealing with the explosive material that additional sensitizer is needed to bring the explosive back to full strength.

In order to further illustrate our invention, there are presented the following examples in which all parts and percentages are by weight unless otherwise indicated.

Example I

To 84 parts of prilled ammonium nitrate were added 16 parts of a liquid sensitizer comprising 5.8 percent by volume of methyl ethyl ketone; 9.8 percent by volume of acetone; and 84.4 percent by volume of a mixture comprising 30 percent by volume of gasoline and 70 percent by volume of nitromethane.

Columnar propagation and plate dent.—A 12-inch long spiral-fabricated cardboard tube having an interior diameter of two inches and a wall thickness of one-eighth of an inch was filled with the explosive. Following this, a No. 8 electric blasting cap was inserted in the top of the explosive column and the material was detonated. On detonation the entire column exploded and the tube was blown apart along its entire length. In this test, the cardboard tube rested upon a one-inch thick aluminum plate which was backed up with four inches of steel. On detonation it was found that a dent having a maximum depth of 0.145 inch was made in the plate.

Bulk density.—A small sample of the explosive was placed in a graduated cylinder and weighed so as to determine its bulk density. The bulk density was found to be 0.891 gram per cc.

Underwater pressure test.—A one-pound sample of the

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explosive was placed in a polyethylene bag having a cylindrical shape. The bag was about three inches in diameter and had a length of approximately five inches. After inserting the explosive in the bag, a Du Pont E-83 detonator containing a base charge of 13.5 grams of pentaerythritol tetranitrate (PETN) was placed in the approximate center of the explosive charge and the charge was placed in a cylindrical tank having a diameter of 20 feet and filled with water. Approximately four inches from the wall of the tank was placed a transducer at a location which was approximately six feet below the water level and about four feet from the bottom of the tank. The charge was placed at the same depth as the transducer and approximately six feet from it along the major diameter of the tank. The transducer was connected to an oscilloscope which was calibrated to read the pressure produced in the tank. On explosion of the charge a peak underwater pressure of 5400 pounds per square inch (p.s.i.) was recorded.

Impact sensitivity (Bureau of Mines).—A 20 milligram (mg.) sample of explosive was tested by the standard Bureau of Mines impact sensitivity apparatus as generally defined in U.S. Bureau of Mines Bulletin 346 (1931). The test involved dropping a two kilogram weight a measured distance against a 20 mg. sample of explosive. The results obtained are reported in terms of the minimum height at which the explosive detonated 100 percent of the time; the minimum height at which the explosive detonated 50 percent of the time; and the maximum height at which the explosive detonated 0 percent of the time. The explosive did not detonate at heights up to 100 cm. with the 2 kilogram weight, which was the limit of calibration with the Bureau of Mines sensitivity apparatus.

Example II

To 84 parts of prilled ammonium nitrate were added 16 parts of a liquid sensitizer comprising 5.8 percent by volume of methyl ethyl ketone, 9.8 percent by volume of acetone, and 84.4 percent by volume of a mixture comprising 70 percent by volume of nitromethane and 30 percent by volume of a high boiling aromatic (sold by Humble Oil & Refining Co. as Aromatic HB and comprising the residual distillation product from Louisiana Crude Oil). The explosive was then subjected to several tests as described in Example I. It detonated completely in the two-inch columnar propagation test, and a one-pound sample produced 10,500 p.s.i. in the underwater explosion test. The explosive would not detonate at a height of 100 cm. (the limit of calibration) with the Bureau of Mines impact sensitivity apparatus.

Example III

To 84 parts of prilled ammonium nitrate were added 16 parts of acetone to give an explosive having a bulk density of 0.862 gram per cc. A sample was inserted in a twelve-inch long steel pipe having a wall thickness of $\frac{1}{4}$ inch and an inside diameter of two inches. The bottom of the pipe was taped shut and the explosive was detonated with a No. 8 electric blasting cap pressed into the top of the explosive at a point lying along the longitudinal axis of the pipe. The explosive was found to fire completely.

When Example III was repeated using cyclohexanone in place of acetone, the explosive composition obtained detonated completely in the two-inch I.D. steel pipe and had a bulk density of 0.862 gram per cc. Other explosives were formed by using still other ketones as the liquid sensitizer in the manner of Example III. For example, we formed explosives containing 84 percent by weight of ammonium nitrate prills and 16 percent by weight of methyl isoamyl ketone, methyl isobutyl ketone, or methyl ethyl ketone. These explosives all had a bulk density of 0.891 gram per cc.

When Example I is repeated using a homogeneous solution of a liquid hydrocarbon such as benzene or

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hexane with nitromethane (without a coupling agent) good explosives are obtained. About 12 to 24 percent of the liquid hydrocarbon is generally present with the liquid nitroalkane to form the homogeneous sensitizer.

When Example II is repeated using other liquid hydrocarbons such as fuel oil, kerosine, hexane, heptane, toluene, xylenes (pure or mixed), or isooctane similar explosives are obtained. Likewise, when other coupling agents such as diisopropyl ether, butyl alcohol, diethyl ether, and dibutyl ketone are used in place of the methyl ethyl ketone of Example II, good explosives are obtained.

In still other of our explosives, when the percentage of the liquid sensitizer is varied from 25 to 100 percent of the saturation amount for the ammonium nitrate prills, good explosives are obtained.

Preferably, the viscosity of the liquid sensitizer is less than about 125 Saybolt seconds Universal (SSU) at about 100° F.

As set forth in the foregoing description, our explosives generally serve a dual function since they can be used in place of dynamite but yet at the same time are cheaper than dynamite on a pound-for-pound basis and from a cost effectiveness standpoint cheaper than ammonium nitrate-fuel oil mixtures. Further, our explosives are readily formed in the field and are composed of ingredients that are not in themselves explosives. Thus, the ingredients forming our explosives can be shipped and stored as ordinary articles of commerce. This results in our explosive being both cheap and safe to ship and store.

In addition to being cheap and safe, our explosives are quite powerful. Thus, it has been observed in field testing that our explosives are more powerful than dynamite. This, coupled with their free flowing properties and ability to detonate in small diameter bore holes, makes them admirably suitable for a number of applications in which dynamite is presently employed.

Our explosives cannot directly replace dynamite since some dynamites can be ignited under water or in wet bore holes. In contrast, our explosives are rendered ineffective by coming in contact with water. This does not present a serious problem, however. When it is desired to use our explosives in applications where they come in contact with water, they can be placed in a water repellent container such as the polyethylene bag employed in the underwater explosion test.

Having fully defined our explosive compositions and their mode of preparation, we desire to be limited only within the lawful scope of the appended claims.

We claim:

1. An explosive composition consisting essentially of prilled ammonium nitrate and a homogeneous liquid sensitizer selected from the group consisting of a liquid hydrocarbon in admixture with a liquid mononitroalkane having the formula $R-NO_2$ where R is a lower alkyl group; a mixture of liquid hydrocarbon with a liquid mononitroalkane having the formula $R-NO_2$ where R is a lower alkyl group and a coupling agent which solubilizes said liquid hydrocarbon and said mononitroalkane, having the formula $R-NO_2$ to form a true solution; and a ketone, said explosive composition having an oxygen balance ranging from about -25 to about +25.

2. An explosive composition consisting essentially of ammonium nitrate prills which are from about 25 to about 100 percent saturated with a homogeneous liquid sensitizer selected from the group consisting of a liquid hydrocarbon in admixture with a liquid mononitroalkane having the formula $R-NO_2$ where R is a lower alkyl group; a mixture of a liquid hydrocarbon with a liquid mononitroalkane having the formula $R-NO_2$ where R is a lower alkyl group and a coupling agent which solubilizes said liquid hydrocarbon and said mononitroalkane, having the formula $R-NO_2$ to form a true solution; and a ketone, said explosive composition having an oxygen balance ranging from -25 to about +25.

3. The explosive composition of claim 1 wherein the

homogeneous liquid sensitizer contains a liquid hydrocarbon in admixture with a liquid mononitroalkane having the formula $R-NO_2$ where R is a lower alkyl group.

4. The explosive composition of claim 1 wherein said homogeneous liquid sensitizer contains a mixture of a liquid hydrocarbon with a liquid mononitroalkane having the formula $R-NO_2$ where R is a lower alkyl group and a coupling agent which solubilizes said liquid hydrocarbon and said mononitroalkane, having the formula $R-NO_2$ to form a true solution.

5. The explosive composition of claim 1 wherein said liquid sensitizer is a ketone.

6. The composition of claim 3 wherein said nitroalkane is nitromethane.

7. The explosive composition of claim 4 wherein said coupling agent is a ketone.

8. The composition of claim 7 wherein said lower nitroalkane is nitromethane.

9. The composition of claim 7 wherein said coupling agent is methyl ethyl ketone.

10. The composition of claim 7 wherein said coupling agent is a mixture of methyl ethyl ketone and acetone.

11. The composition of claim 5 wherein said ketone is a dialkyl ketone.

12. The composition of claim 11 wherein said alkyl groups in said dialkyl ketone are lower alkyl groups.

13. The composition of claim 12 wherein said ketone is methyl ethyl ketone.

14. A method for forming an explosive comprising adding to prilled ammonium nitrate a homogeneous liquid

sensitizer selected from the group consisting of a liquid hydrocarbon in admixture with a liquid mononitroalkane having the formula $R-NO_2$ where R is a lower alkyl group, a liquid hydrocarbon with a liquid mononitroalkane having the formula $R-NO_2$ where R is a lower alkyl group and a coupling agent which solubilizes said liquid hydrocarbon and said mononitroalkane, having the formula $R-NO_2$ to form a true solution, and a ketone until said prilled ammonium nitrate is essentially saturated.

15. The composition of claim 14 wherein said coupling agent is a mixture containing benzene, naphthalene, and acetone.

16. An explosive composition consisting essentially of prilled ammonium nitrate, nitromethane, and an aromatic liquid hydrocarbon, said explosive composition having an oxygen balance ranging from about -25 to about +25.

17. The explosive composition of claim 16 in which said liquid hydrocarbon is toluene.

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